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(54) METHOD FOR MANUFACTURING CYCLIC OLEFIN POLYMER

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for manufacturing a cyclic olefin polymer showing heat resistance and lowering of the molecular weight and having little residual solvent.
SOLUTION: A cyclic olefin polymer composition comprising a cyclic olefin polymer and an organic solvent is subjected to (1) heating with agitation at ≥20° C and not more than the boiling point of the composition under normal pressure, and then to heating under reduced pressures with continued agitation in a stepwise manner of (2) at ≥80° C and ≤255° C under a pressure of ≥4 kPa and ≤70 kPa and (3) at ≥190° C and ≤255° C under a pressure of ≥1 kPa and <4 kPa. The organic solvent in the composition is thus eliminated and the polymer showing little degradation of heat resistance and lowering of the molecular weight and having little residual organic solvent can be obtained.

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CLAIMS

[Claim(s)]
[Claim 1] Stirring the annular olefin system polymer constituent which consists of an annular olefin system polymer and an organic solvent (1) By ordinary pressure, below the boiling point of a temperature the constituent of 20 degrees C or more, 70 or less kPa of (2) 4 or more kPas pressures, The manufacture approach of the temperature of 255 degrees C or less of 80 degrees C or more, less than 4 kPa of (3) pressures of 1Pa or more, and the annular olefin system polymer characterized by removing scale loss aggressiveness and this organic solvent gradually with 190 degrees C or more 255 degrees C or less.
[Claim 2] The manufacture approach of an annular olefin system polymer according to claim 1 that this organic solvent is the aliphatic hydrocarbon of carbon numbers 5-14, the aromatic hydrocarbon of carbon numbers 6-14, or oxygenated aliphatic hydrocarbon of carbon numbers 1-10.
[Claim 3] The manufacture approach of an annular olefin system polymer according to claim 1 that the reduced viscosity measured at 30 degrees C among the toluene solution of concentration 0.5 g/dL of this annular olefin system polymer is 0.15 or more dL/g 1.5 or less dL/g.
[Claim 4] The annular olefin system polymer obtained by the manufacture approach given in any 1 term of claim 1 - claim 3.
[Claim 5] The optical material which mainly becomes any 1 term of claim 1 - claim 3 from the annular olefin system polymer obtained by the manufacture approach of a publication.
[Claim 6] The medical ingredient which mainly becomes any 1 term of claim 1 - claim 3 from the annular olefin system polymer obtained by the manufacture approach of a publication.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to an annular olefin system polymer and its manufacture approach. It is related with the molding material which it mainly comes to carry out from the manufacture approach of an annular olefin system polymer that remove this organic solvent, without causing a fall for the heat-resistant fall of the this annular olefin system polymer from the annular olefin system polymer constituent which consists of an annular olefin system polymer and an organic solvent in more detail, and molecular weight, and this organic solvent hardly remains, the annular olefin system polymer obtained by it, and this annular olefin system polymer. This annular olefin system polymer is suitable for the medical ingredient application according by optical homogeneity and high transparency to optical material applications including an optical disk substrate and high transparency, and low moisture permeability.
[0002]
[Description of the Prior Art] Various properties, such as high transparency, optical isotropy (low form birefringence), dimensional stability, weatherability, and thermal stability, are required of the plastics used for optical materials, such as an optical disk. Moreover, the polycarbonate used regularly conventionally and a polymethyl methacrylate have a fault as shown below with progress of the densification of a record ingredient. The rate of a proper birefringence being large and an optical anisotropy's tending to produce the former in a moldings and the latter are that it is lacking in dimensional stability since water absorption is very high, and thermal resistance is also low. These faults will become remarkable, so that information is recorded on high density. In view of this situation, development of an annular olefin system polymer is briskly performed as alternate material, such as a polycarbonate. After these polymers copolymerize an alpha olefin, annular olefins, etc., such as ethylene or a propylene, with what hydrogenated the partial saturation double bond produced in a polymer after carrying out ring opening polymerization of the annular olefin etc. according to ** metathesis catalyst, ** Ziegler-Natta catalyst, or a metallocene catalyst, without carrying out ring breakage of the annular olefin etc., they are divided roughly into what hydrogenated the partial saturation double bond, and the thing which hydrogenated the partial saturation double bond containing the aromatic series of the polymer which uses ** polystyrene as a principal component (**). These polymers are obtained mainly by the polymerization reaction and the hydrogenation reaction performed succeedingly in a solution system, and are obtained in many cases as an annular olefin system polymer constituent which consists of an annular olefin system polymer and an organic solvent immediately after a reaction. In order to obtain the annular olefin system polymer made into the

purpose from this constituent, it is necessary to remove an organic solvent from this constituent.
[0003] As an approach of removing this solvent from the constituent which generally consists of an olefin polymer and a solvent A) The polymer constituent heated under pressurization or ordinary pressure Below the melting point of this polymer The approach (JP,57-139107,A, USP3544540 grade) of removing a solvent, and the method (WO99-32525 grade) of heating a polymer constituent in B container and removing a solvent are well-known by injecting in the container under ordinary pressure or reduced pressure. A) It is applied mainly to crystalline polyethylene and law is difficult desolventization in the annular polyolefine with comparatively easy desolventization which is amorphism nature. On the other hand, although B law is applied to amorphous polyolefine, generally it is the conditions for a polymer with a low glass transition temperature, and when it applies to an annular olefin system polymer as it is, we are anxious about a lot of solvents remaining. Moreover, if it heats further, the temperature of a constituent is raised and a solvent is removed in order to lessen a residual solvent, we will be anxious about the heat deterioration component in this polymer increasing with heating, and a fall and a heat-resistant fall of molecular weight taking place.
[0004] The annular olefin system polymer is suitable for optical material applications including an optical disk substrate by optical homogeneity and high transparency. however, the heat deterioration component of this polymer -- coloring of a polymer and the problem of a heat-resistant fall -- moreover, problems accompanying desolventization, such as curvature and a surface sink, produce the organic solvent which remained superfluously at the time of the fall of the heat deflection temperature of this polymer, and shaping.
[0005] Moreover, as for the annular olefin system polymer, use is also expected as the container and packing material in a physic medical-application way from the high transparency and low moisture permeability. We are anxious about the problem of the contamination to the perimeter according [the organic solvent which remained superfluously / coloring of a polymer or the problem of a fall of dynamics physical properties / again / as for the heat deterioration component of this polymer] to exudation.
[0006]
[Problem(s) to be Solved by the Invention] This invention has few heat-resistant falls and falls of molecular weight, and a residual solvent aims at offer of the optical material obtained from the manufacture approach of little annular olefin system polymer, the annular olefin system polymer obtained by the approach, and this polymer, and a medical ingredient.
[0007]
[Means for Solving the Problem] There are few falls of thermal resistance [situations / above] and falls of molecular weight, and manufacture of an annular olefin system polymer with few residual solvents is indispensable, and it is wished. As a result of inquiring wholeheartedly in view of this situation, by decompressing and/or heating gradually the annular olefin system polymer constituent which consists of the above-mentioned annular olefin system polymer and an organic solvent, stirring, we do not almost have a heat-resistant fall and found out the manufacture approach of an annular olefin system polymer with them. [few / the amount of residual solvents is remarkable and] It is few, and the amount of residual solvents is remarkable, and the molding material which mainly becomes about the annular olefin system polymer obtained by this manufacture approach and this polymer has few heat-resistant falls and falls of molecular weight. Therefore, the mold goods fabricated from this molding material have neither curvature nor a surface sink, and there are still few worries about the contamination to the

perimeter by solvent exudation. We came to propose this invention from the above knowledge.
[0008] Namely, this invention, stirring the annular olefin system polymer constituent which consists of an annular olefin system polymer and an organic solvent (1) By ordinary pressure, below the boiling point of a temperature the constituent of 20 degrees C or more, 70 or less kPa of (2) 4 or more kPas pressures, It is the manufacture approach of the annular olefin system polymer characterized by removing scale loss aggressiveness and this organic solvent gradually with the temperature of 255 degrees C or less of 80 degrees C or more, (3) pressures of less than 4 kPa of 1Pa or more, and 190-degree-C or more temperature of 255 degrees C or less. Furthermore, this invention contains little annular olefin system polymer of a residual organic solvent with few heat-resistant falls obtained by the above-mentioned manufacture approach. Furthermore, this invention offers the optical material and medical ingredient which mainly consist of an annular olefin system polymer with few residual organic solvents obtained by the above-mentioned manufacture approach.
[0009]
[Embodiment of the Invention] In this invention, as an annular olefin system polymer used ** After carrying out ring opening polymerization of the annular olefin etc. according to a metathesis catalyst, with the hydrogenation ring-opening-polymerization object which hydrogenated the partial saturation double bond produced in a polymer, ** Ziegler-Natta catalyst, or a metallocene catalyst After copolymerizing an alpha olefin, annular olefins, etc., such as ethylene or a propylene, without carrying out ring breakage of the annular olefin etc., It is divided roughly into the hydrogenation styrene system polymer and hydrogenation styrene system copolymer which hydrogenated the partial saturation double bond containing the aromatic series of the addition mold copolymer which hydrogenated the partial saturation double bond if needed, the polymer which uses ** polystyrene as a principal component, or a copolymer.
[0010] ** A hydrogenation ring-opening-polymerization object is acquired by hydrogenation of the ring-opening-polymerization object which is a precursor. A ring-opening-polymerization object is acquired by generally carrying out the polymerization of the annular olefin etc. under existence of a metathesis catalyst. These are indicated by JP,60-26024,A, JP,63-218726,A, JP,2-133413,A, JP,3-109418,A, etc. As a monomer used, norbornene, 5-phenyl norbornene, Tetracyclo [4, 4, 0, 12, 5, 17, 10] -3 dodecen, Annular monoene one, such as 8-phenyl tetracyclo [4, 4, 0, 12, 5, 17, 10] -3 dodecen, Cyclo BENTA diene, a dicyclopentadiene, norbornadiene, 5-ethylidene norbornene, Annular dienes, such as 8-ethylidene tetracyclo [4, 4, 0, 12, 5, 17, 10]-3-dodecen and 8-isopropylidene tetracyclo [4, 4, 0, 12, 5, 17, 10]-3-dodecen, are used preferably. When the availability of a raw material and the thermal resistance of a polymer are taken into consideration especially, norbornene, tetracyclo [4, 4, 0, 12, 5, 17, 10] -3 dodecen, and especially a dicyclopentadiene are desirable.
[0011] A C=C double bond is included in the acquired ring-opening-polymerization object unescapable. A polymer including a C=C double bond is lacking in thermochemistry stability, and does not bear practical use. Therefore, it is necessary to hydrogenate a ring-opening-polymerization object further under existence of a hydrogenation catalyst. Especially the hydrogenation approach of a ring-opening-polymerization object should just be an approach which is not limited but can hydrogenate a C=C double bond efficiently. Generally it hydrogenates in an inert solvent and under hydrogen pressurization under existence of a hydrogenation catalyst. The aromatic hydrocarbon of the carbon numbers 6-14, such as aliphatic hydrocarbon; benzene of the carbon numbers 5-14, such as a hexane, a heptane, an

octane, a dodecane, a cyclohexane, cycloheptane, a cyclo decane, and a methylcyclohexane, toluene, a xylene, and ethylbenzene, is suitably used for an inert solvent, and a cyclohexane, a methylcyclohexane, and toluene are most preferably used for it among these. The homogeneous catalyst of the halogenide of IV groups, such as the solid-state catalyst which supported the metal of VIII groups, such as nickel, palladium, platinum, cobalt, a ruthenium, and a rhodium, or its compound to porous support, such as carbon, an alumina, a silica, a silica alumina, and diatomaceous earth, as a hydrogenation catalyst or vanadium, chromium, manganese, iron, a ruthenium, cobalt, nickel, and palladium, - a VIII group, an acetylacetonate complex, a carboxylate complex, a NAFUTETO complex, a trifluoroacetate complex a stearate complex, be mentioned In these, it is desirable especially to use a homogeneous catalyst.

[0012] ** the addition mold copolymer copolymerized an alpha olefin and annular olefins, such as ethylene or a propylene, without carrying out ring breakage of the annular olefin -- come out. These are indicated by JP,60-168708,A, JP,61-115916,A, JP,61-221206,A, JP,61-292601,A, etc. As an annular olefin, norbornene, 5-phenyl norbornene, Tetracyclo [4, 4, 0, 12, 5, 17, 10] -3 dodecen, Annular monoene one, such as 8-phenyl tetracyclo [4, 4, 0, 12, 5, 17, 10] -3 dodecen, Cyclo BENTA diene, a dicyclopentadiene, norbornadiene, 5-ethylidene norbornene, Annular dienes, such as 8-ethylidene tetracyclo [4, 4, 0, 12, 5, 17, 10]-3-dodecen and 8-isopropylidene tetracyclo [4, 4, 0, 12, 5, 17, 10]-3-dodecen, are used suitably. If the availability of a raw material and the thermal resistance of a polymer are taken into consideration especially, norbornene, tetracyclo [4, 4, 0, 12, 5, 17, 10]-3-dodecen, and especially a dicyclopentadiene are suitable. Among them, since a generation polymer includes a C=C double bond when annular diene is used, it is desirable to hydrogenate an addition polymer further like the manufacture approach of a hydrogenation ring-opening-polymerization object, as mentioned above.

[0013] Moreover, as an alpha olefin, the alpha olefin of the carbon numbers 3-14, such as a propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, and 1-dodecen, is used. Although the ethylene from reactivity is the most desirable as an annular olefin and a monomer to copolymerize, a propylene is also used preferably. These may be used independently or may be combined two or more kinds. Generally this addition polymer is easily compoundable under existence of Ziegler-Natta catalyst or a metallocene catalyst.

[0014] ** A hydrogenation styrene system polymer and a hydrogenation styrene system copolymer perform a hydrogenation reaction to the partial saturation double bond containing the aromatic series of the polymer which uses polystyrene as a principal component, or a polystyrene system copolymer. These are easily obtained by generally hydrogenating a styrene system polymer and/or a styrene system copolymer. As a styrene monomer used for a styrene system polymer, styrene, alpha methyl styrene, p-methyl styrene, vinyl naphthalene, etc. are mentioned. Among this, the styrene from availability and polymer physical properties is the most desirable, and that polymer is polystyrene.

[0015] On the other hand, as a copolymerization component of a styrene system polymer, dienes, such as 1,3-butadiene, isoprene, 2, 3-dimethylbutadiene, 2, 3-pentadiene, 2, and 3-hexadiene, are used preferably. By introducing these copolymerization components, dynamics physical properties can be raised remarkably, without spoiling the transparency of the annular polymer made into the purpose. An isoprene and 1,3-butadiene are preferably used from the field of polymerization activity and economical efficiency also in these. These may be used independently, and two or more kinds may be used together and they may be used. As for the rate of the conjugated diene component in this styrene-conjugated diene copolymer, it is desirable that it is in 30 or less % of the weight of the range 1% of the weight or more. A

conjugated diene component is 2-% of the weight or more 25 or less % of the weight of the range more preferably. It is not desirable in order to spoil transparency it not only to to spoil the thermal resistance of an annular olefin system polymer, but, if the rate of a conjugated diene component cannot raise dynamics properties, such as shock resistance, at 1 or less % of the weight and exceeds 30 % of the weight.

[0016] Especially limitation does not have the manufacturing method of these styrene system polymers and a styrene system copolymer, and a general radical polymerization method, an anionic polymerization method, a cationic polymerization method, etc. are used preferably. Moreover, a random copolymer, a block copolymer, a radial block copolymer, etc. are mentioned as a joint format of the styrene system copolymer which introduced the copolymerization component into the styrene system polymer. A radial block copolymer has the inner radial configuration of a block copolymer, and a radial configuration shows a configuration to which several polymer chains were extended from the core to the radial. In thinking thermal resistance as important, especially when a block copolymer thinks the fluidity at the time of shaping as important among these again, a radial block copolymer is desirable. What is necessary is to judge these suitably according to an application and just to adopt them.

[0017] Especially the hydrogenation approach of a styrene system polymer and a styrene system copolymer should just be an approach which is not limited but can hydrogenate aromatic series and a C=C double bond efficiently. Generally, the inside of an inert solvent and the bottom of hydrogen pressurization are performed under existence of a hydrogenation catalyst, and it hydrogenates at an elevated temperature. The aliphatic hydrocarbon of the carbon numbers 5-14, such as a hexane, a heptane, an octane, a dodecane, a cyclohexane, cycloheptane, a cyclo decane, and a methylcyclohexane, is suitably used for an inert solvent, and a cyclohexane and a methylcyclohexane are most suitably used for it among these. The homogeneous catalyst of the halogenide of IV groups, such as the solid-state catalyst which supported the metal of VIII groups, such as nickel, palladium, platinum, cobalt, a ruthenium, and a rhodium, or its compound to porous support, such as carbon, an alumina, a silica, a silica alumina, and diatomaceous earth, as a hydrogenation catalyst or vanadium, chromium, manganese, iron, a ruthenium, cobalt, nickel, and palladium, - a VIII group, an acetylacetonate complex, a carboxylate complex, a NAFUTETO complex, a trifluoroacetate complex a stearate complex, be mentioned Activity is highly used for what supported nickel, palladium, and platinum to a silica, a silica alumina, and diatomaceous earth preferably among these. These hydrogenation catalysts may be used independently, or it may combine and they may be used.

[0018] Molecular weight of this polymer is made to express using the reduced viscosity (etasp/C) which is a typical scale showing molecular weight. When the mechanical strength and fabrication nature of a molding material are taken into consideration, among the concentration of 0.5g / toluene solution of dL, in the reduced viscosity measured at 30 degrees C, the thing of the 0.15 or more dL/g range of 1.5 or less dL/g is desirable, and is 0.3 or more dL/g0.8 dL/g preferably [it is more desirable and] to the range of 0.2 or more dL/g1.0 dL/g, and a pan. If average molecular weight is lower than 0.15 dL/g, mechanical strengths run short, when higher than 1.5 dL/g, melt viscosity is too high, a fluidity runs short, and shaping becomes difficult and is not desirable.

[0019] The annular olefin system polymer constituent which consists of the annular olefin and organic solvent in this invention is a solution which consists of this annular olefin polymer from which a part for metallic calxes, such as catalyst residue, was removed, and an organic solvent after composition by the solution system of the above-mentioned **, **, and **.

[0020] this organic solvent may be an organic solvent used in the synthetic process of the above-mentioned **, **, and **, and may be the oxygenated aliphatic hydrocarbon of the carbon numbers 1-10, such as the aromatic hydrocarbon; methanol of the carbon numbers 6-14, such as aliphatic hydrocarbon; benzene of the carbon numbers 5-14, such as a hexane, a heptane, an octane, a dodecane, a cyclohexane, cycloheptane, a cyclo decane, and a methylcyclohexane, toluene, a xylene, and ethylbenzene, ethanol, diethylether, methyl tertiary butyl ether, a tetrahydrofuran a furan, and a pyran, and the mixture of these arbitration. Toluene, a cyclohexane, a methylcyclohexane, and methyl tertiary butyl ether are preferably mentioned also in them.

[0021] The annular olefin system polymer constituent in this invention Even if it condenses beforehand and uses by a rotary evaporator etc., again Although you may dilute with the organic solvent mentioned by the term of the above-mentioned organic solvent, 5 - 60 % of the weight of annular olefin system polymers, They are the constituent which consists of 40 - 95 % of the weight of organic solvents, the constituent which consists of 10 - 50 % of the weight of annular olefin system polymers, and 50 - 90 % of the weight of organic solvents preferably, and the constituent which consists of 15 - 40 % of the weight of annular olefin system polymers, and 60 - 85 % of the weight of organic solvents still more preferably. If the presentation of an annular olefin polymer exceeds 60 % of the weight, the fluidity of an annular olefin system polymer constituent is scarce, and at less than 5 % of the weight, this presentation has the low yield of an annular olefin system polymer, and is not [both] desirable.

[0022] In order to control still more effectively the fall of the molecular weight by heat deterioration in this invention, it is desirable to add the stabilizer for pyrolysis prevention in an annular olefine copolymer. All of the hindered phenol system stabilizer generally marketed as a stabilizer, a lactone system stabilizer, and a phosphite system stabilizer etc. are usable, and its combination of such arbitration is also usable. inside -- desirable -- a hindered phenol system stabilizer -- the stabilizer of a hindered phenolic group content acrylate compound is more preferably desirable. 500 ppm or more 50000 ppm or less of 1000 ppm or more 30000 ppm or less of these stabilizers are preferably used in [2000 ppm or more] 20000 ppm or less still more preferably to a polymer. Since [neither of] this stabilizer becomes Hayes of an annular olefin system polymer, and the cause of coloring for it to be 50000 ppm or more and effectiveness becomes inadequate in 500 ppm or less, it is desirable.

[0023] With the thing in this invention for which this organic solvent is removed gradually By (1) ordinary pressure, stirring this annular olefin system polymer constituent Below the boiling point of a temperature the constituent of 20 degrees C or more (2) It is evaporating scale loss aggressiveness and this organic solvent gradually with 4 or more kPas of pressures of 70 or less kPa, the temperature of 255 degrees C or less of 80 degrees C or more, (3) pressures of 4 or less kPa of 1Pa or more, and 190-degree-C or more temperature of 255 degrees C or less, and removing.

[0024] (1) is the phase where a solvent is removed most and it is desirable to carry out below in the boiling point of this constituent under atmospheric pressure. It solidifies, while this polymer constituent will foam, if it carries out under reduced pressure, and about [that it becomes impossible to stir] or a solvent tends to remain in foam, and it is not desirable. temperature -- below the boiling point of the more than boiling point minus 10 degree-C constituent of this constituent -- desirable -- more than boiling point minus 5 degree C of a constituent -- below the boiling point is more desirable. Since solvent removal effectiveness becomes low, it is not desirable less than [of the constituent which requires temperature / boiling point minus 10

degree C]. The polymer concentration contained in the constituent after concentration has 85 or less desirable % of the weight 50 % of the weight or more, and it is 80 or less % of the weight 60 % of the weight or more more preferably. If polymer concentration exceeds 85 % of the weight, it becomes impossible to stir by viscosity's becoming high or solidifying, and polymer concentration is [neither of that the solvent removal effectiveness in the 2nd step becomes low at less than 60 % of the weight, or it foams and is easy to solidify in the 2nd step] desirable.
[0025] (2) is the phase where most solvents are removed and 4 or more kPas of pressures of 70 or less kPa and its 80-degree-C or more temperature of 255 degrees C or less are desirable. If a pressure exceeds 70kPa(s), a solvent will be hard to be removed, and in less than 4 kPas, this solvent does not be [it foams and] easy to solidify and have a desirable pressure. On the other hand, if temperature exceeds 255 degrees C, the heat deterioration component of an annular olefin system polymer will increase, and the viscosity of this polymer solution is too high of stopping to stir at less than 80 degrees C, a solvent is not only hard to be removed, but, and it is not desirable. The polymer concentration contained in the constituent after this concentration phase is larger than 85 % of the weight, and 99.5 or less % of the weight is desirable, and it is 99 or less % of the weight 90 % of the weight or more more preferably. or [that viscosity will become high as well as the phase of (1) if polymer concentration exceeds 99.5 % of the weight] -- or by solidifying, stirring becomes impossible, polymer concentration becomes low at less than 85 % of the weight, and the solvent removal effectiveness in the 3rd step is not desirable.
[0026] (3) is the phase where a solvent is removed by altitude and the pressure of 4 or less kPa of 1Pa or more and its 190-degree-C or more temperature of 255 degrees C or less are desirable. Since the device which a solvent is hard to be removed and adjusts a pressure in less than 1Pa will become expensive if a pressure exceeds 4kPa(s), it is not economically realistic, and it is not desirable. On the other hand, if temperature exceeds 255 degrees C, the heat deterioration component of an annular olefin system polymer will increase, and the viscosity of this polymer solution is too high of stopping to stir at less than 190 degrees C, a solvent is not only hard to be removed, but, and it is not desirable. It is suitable also from a viewpoint of diffusion of a solvent to carry out about this solvent removal, stirring an annular olefin system polymer solution. Moreover, less than 30 minutes has [duration 230 degrees C or more] desirable temperature about (2) or (3) phase, and less than 20 more minutes is desirable. In 30 minutes or more, since duration 230 degrees C or more arises remarkably, temperature of heat deterioration is not [duration] desirable.
[0027] 500 ppm or less are desirable still more desirable, and the residual organic **** agent of the annular olefin system polymer obtained in this way is 200 ppm or less. In 500 ppm or more, the fall of glass transition temperature becomes about 5 degrees C or more, and the amount of residual organic solvents is not desirable from a heat-resistant viewpoint. Moreover, 0.06 or less are desirable still more desirable, and the fall of etasp/C accompanying heat deterioration is 0.03 or less. If the fall of etasp/C exceeds 0.06, it becomes impossible to attain the dynamics physical properties originally designed, and is not desirable. etasp/C said here is the reduced viscosity in 30 degrees C of the 0.5 g/dL toluene solution of an annular olefin system polymer.
[0028] The optical material and medical ingredient which consist of an annular olefin system polymer with few residual organic solvents obtained in this way can be fabricated by the well-known fabricating methods, such as the melting fabricating methods, such as injection molding and extrusion molding. Especially injection molding can be used suitable for manufacture of an optical disk substrate.

[0029]

[Effect of the Invention] According to this invention, there is little heat deterioration and an annular olefin system polymer with few residual organic solvents and its optical material, and a medical ingredient are obtained. Consequently, the annular olefin system polymer with few residual organic solvents does not have to carry out desolventization, such as desiccation, at the time of a product final process or shaping. Moreover, the outstanding optical material and outstanding medical ingredient which do not have the heat-resistant fall accompanying the fall of the heat deflection temperature by the residual solvent about the obtained molding material, and do not have physical instability, such as a dimensional change accompanying desolventization, an environmental load, etc. can be offered.

[0030]

[Example] This invention is explained in full detail according to an example below. However, this invention is not limited to these examples at all.

[0031] All (DCPD) of a cyclohexane, toluene, styrene, an isoprene, and a dicyclopentadiene used what performed distillation purification and was fully dried.

[0032] The annular olefin system polymer used for measurement in the example of reference was isolated as follows. That is, reduced pressure drying of this polymer slurry of an annular olefin system polymer constituent that reprecipitated and obtained the part in isopropanol very much was carried out at filtration and 60 degrees C for 5 hours, and the flake-like annular olefin system polymer was obtained. In (2) or (3) phase, the temperature of each duration 230 degrees C or more was the range for 15 or less minutes 10 minutes or more among the phases of above-mentioned (1) - (3) performed in the example.

[0033] The parameter performed in the example, the example of reference, and the example of a comparison was measured by the following approaches.

1) Product made from styrene molar fraction, DCPD molar fraction, and rate of hydrogenation:JEOL EX-270 mold nuclear-magnetic-resonance-absorption equipment was used, deuteration chloroform was used as the solvent, and the quantum of the 1 H-NMR measurement was performed and carried out in ordinary temperature by making a tetramethylsilane into an internal standard.

2) Glass-transition-temperature (Tg):TA Product made from Instruments The 2920 mold DSC was used and the programming rate was measured by part for 20-degree-C/.

3) Reduced viscosity : the reduced viscosity (etasp/C) in 30 degrees C of the toluene solution of concentration 0.5 g/dL was measured.

4) The amount of residual solvents : the sample was prepared and measured as follows using the GC[by Shimadzu Corp.]-5A mold gas chromatography (GC). the case where a residual solvent is a cyclohexane -- a 0.5g polymer -- the object for analysis -- the toluene solution which was dissolved in toluene [HPLC grade made from Kanto Chemistry] 9.5g, and was obtained -- the object for analysis -- in addition to isopropanol [HPLC grade made from Kanto Chemistry] 20g, the polymer component was reprecipitated. The obtained mixture was filtered and filtrate was made into the sample. When a solvent was toluene, the polymer was dissolved in the cyclohexane for analysis [the HPLC grade made from Kanto Chemistry], and also the sample was prepared similarly.

5) Light transmission : the ultraviolet [by Shimadzu Corp.] visible spectroscope (UV-240) was used.

6) Hayes value : automatic [by Nippon Denshoku Industries Co., Ltd.] digital hazemeter UDH-20D was used.

7) Polymer concentration : the initial concentration of a polymer was computed by having taken and heated some polymer solutions created in the example of reference, and having removed the solvent. It computed from the amount of solvents removed based on this value.

[0034] [example 1 of reference] BASF, and the polystyrene GP158 made from AG -- from silica-alumina support nickel catalyst [Aldrich, as it was the following about K, using purchase and 65 % of the weight [of rates of nickel support]] as the inside of a cyclohexane solvent, and a catalyst, the hydrogenation reaction was performed.

[0035] The autoclave made from stainless steel of capacity 10with electromagnetic-mixing aerofoil L was used for the reaction container. the inside of a container -- this polystyrene 750g and cyclohexane [-- Wako Pure Chem Industry -- purchase]2200g and methyl-tertiary-butyl-ether [-- from Kanto Science, purchase]1500g and 118g of these silica-alumina support nickel catalysts were taught, and nitrogen gas and after hydrogen gas subsequently permuted, the hydrogenation reaction was performed for the inside of a container by 180 degrees C and hydrogen pressure 10MPa for 160 minutes. After cooling a container to near ordinary temperature, the inside of a container was returned to ordinary pressure, the nitrogen purge of the inside of a container was carried out further, and hydrogenation polystyrene and a cyclohexane solution including a silica-alumina support nickel catalyst were obtained. This solution was filtered with the membrane filter of the bottom of the nitrogen pressurization of 0.4MPa(s), and 0.1 micrometers of pore size, the silica-alumina support nickel catalyst was removed, and 4200g of transparent and colorless hydrogenation polystyrene cyclohexane solutions was obtained.

[0036] Some obtained hydrogenation polystyrene cyclohexane solutions were extracted, and various analysis was performed. One H-NMR analysis to the rate of hydrogenation was 99.0%. DSC measurement to glass transition temperature was 148 degrees C. Among the toluene solution of concentration 0.5 g/dL, reduced viscosity etasp/C measured at 30 degrees C was 0.47 dL/g, and was a value high enough.

[0037] To the [example 2 of reference] metallocene, isopropylidene-(9-fluorenyl) (cyclopentadienyl) zirconium dichloride [iPr(Cp) (Flu) ZrCl2, reference J.A.Ewen et al, J.Am.Chem.Soc., and vol 110 and 6255-6266 (1988) are followed. To synthetic] and a co-catalyst Tosoh Akzo trityl tetrakis (pentafluorophenyl) borate ([(C6H5) 3C]+ [B(C6F5) 4] -), Tosoh Akzo triisobutylaluminum was used for the alkylating agent, and as it was the following, copolymerization reaction of ethylene and DCPD, hydrogenation reaction, and catalyst removal were performed.

[0038] The autoclave made from stainless steel of capacity 3with electromagnetic-mixing aerofoil L was used for the reaction. After nitrogen gas permuted the inside of a container, toluene 1320g, DCPD181g, and triisobutylaluminum solution (n-hexane solution of concentration 1M) 18mL were taught in the container. Next, after raising temperature to 40 degrees C, ethylene fully permuted the inside of a container and dissolution saturation of the ethylene was carried out. Then, 257mg [(C6H5) 3C]+[B(C6F5)4] iPr(- and 122mg) (Cp) (Flu) ZrCl2 was added, and the polymerization was made to start. Supplying ethylene being continued so that the ethylene pressure under polymerization and in a container may hold one atmospheric pressure, and supplying DCPD of this molar quantity to coincidence was continuously continued to the amount of supply of ethylene. 140 minutes after starting a polymerization, the isopropanol of a minute amount was added, the reaction was terminated and 1750g of copolymer constituents was obtained. The amount of ethylene supplied between reactions was 97g, and the amount of DCPD(s) was 168g.

[0039] Some obtained copolymer constituents were extracted and various analysis was performed. The presentation ratio of 1 H-NMR analysis to a DCPD component was 43-mol%. DSC measurement to glass transition temperature was 152 degrees C. Among the toluene solution of concentration 0.5 g/dL, reduced viscosity etasp/C measured at 30 degrees C was 0.70 dL/g, and was a value high enough.

[0040] 3.0g of cobalt tris acetylacetonate complexes and the mixture of triisobutylaluminum solution (n-hexane solution of concentration 1M) 24mL were further added to the obtained copolymer constituent, the hydrogenation reaction was performed for 110 degrees C, hydrogen pressure 4MPa, and 120 minutes, and the transparent hydrogenation copolymer constituent was obtained in yellow. The lactic-acid water solution which consists of 31.8g of lactic acids and 3.2g of water at 100 degrees C was added stirring this hydrogenation copolymer constituent, the homogeneous catalyst was made to condense by stirring at this temperature for 120 minutes, and the muddy peach-colored hydrogenation copolymer constituent was obtained. When this peach-colored hydrogenation copolymer constituent was filtered by the nitrogen pressure of 0.4MPa using the membrane filter of 0.45 micrometers of pore size, 1520g of transparent and colorless hydrogenation copolymer toluene solutions was obtained.

[0041] Some of these hydrogenation copolymer toluene solutions were extracted, and various analysis was performed. One H-NMR analysis to the rate of hydrogenation was 99.9% or more. DSC measurement to glass transition temperature was 149 degrees C. Among the toluene solution of concentration 0.5 g/dL, reduced viscosity etasp/C measured at 30 degrees C was 0.48 dL/g, and was a value high enough.

[0042] 8-ethylidene tetracyclo [4, 4, 0, 12, 5, 17, 10]-3-dodecen 285g, toluene 1100g, 1-hexene 4.2g, triethylamine 7.5g, and triisobutylaluminum 15g were added to the reaction container made from stainless steel of [example 3 of reference] 3L, 2.8g of titanium tetrachlorides was added further, the polymerization was performed at -10 degrees C for 120 minutes, and the ring-opening-polymerization object was acquired. Reduced viscosity etasp/C measured at 30 degrees C was 0.65 dL/g among the toluene solution of 0.5 g/dL of a polymer which carried out little preparative isolation of the obtained solution, and refined it with the conventional method, and the glass transition temperature (Tg) measured using DSC was 186 degrees C.

[0043] It added stirring 7.8g of lactic acids, and 1.0g of water at 100 degrees C in the obtained reaction container, and was made to react by this ** for 120 minutes. Reaction mixture was colored the black slurry which became muddy from dark brown. This slurry was succeedingly applied to filtration processing. Adsorption treatment was carried out for filtrate using the basic alumina, and the processing liquid of transparence was obtained. The solution obtained in this way was added to a lot of ethanol, the precipitate which deposited was dried the ** exception, and the colorless flake was obtained.

[0044] The obtained flake-like solid-state was dissolved in the 1100g toluene introduced into the autoclave made from 5L stainless steel. Nitrogen gas fully permuted the air in the autoclave into which this solution was put. Tris (acetylacetonato) cobalt 3.0g and triisobutylaluminum 4.8g were added in this solution, the hydrogenation reaction was performed for 120 minutes by hydrogen pressure 4.4MPa, and reaction mixture was obtained. The rate of hydrogenation of the polymer which carried out little preparative isolation of this reaction solution, and refined it with the conventional method was 99.9% or more from 1 H-NMR spectrum. Moreover, reduced viscosity etasp/C measured at 30 degrees C using the toluene solution of 0.5 g/dL was 0.55 dL/g, and the glass transition temperature (Tg) measured using DSC was 140 degrees C.

[0045] It added stirring the lactic-acid water solution which contains 17.6g of lactic acids, and

1.8g of water in the obtained reaction mixture at 100 degrees C, and was made to react by this ** for 120 minutes. Reaction mixture was colored the slurry in which pink became muddy from dark brown. This slurry was succeedingly applied to filtration. Adsorption treatment was carried out for the obtained filtrate using the basic alumina, and the transparent and colorless hydrogenation polymer toluene solution was obtained.

[0046] It introduced into the container made from 3L stainless steel equipped with the mechanical stirring aerofoil and the RIBIHHI mold condensator made from stainless steel set as 10 degrees C, after dissolving Sumi Reiser GS[0.4by Sumitomo Chemical Co., Ltd.] g in 1000g of hydrogenation polystyrene cyclohexane solutions obtained in the example 1 of [example 1] reference as a stabilizer. Stirring this polystyrene solution, after carrying out the nitrogen purge of the inside of a container, contents were heated and boiled at ordinary pressure and cyclohexane 850g was made to remove. At this time, polymer concentration was 80 % of the weight. Subsequently, an internal temperature is set as 230 degrees C, and 28g of cyclohexanes was made to remove, adjusting and stirring internal pressure to 25kPa(s) using a vacuum pump. At this time, polymer concentration was 98 % of the weight. The cyclohexane was made to remove for 10 minutes, adjusting internal pressure to 500Pa and stirring a container further, using a vacuum pump, with 230 degrees C. After cooling a container to near the ordinary temperature, nitrogen was introduced, and massive hydrogenation polystyrene 120g was obtained from the inside of a container.

[0047] It was 180 ppm when the quantum of the residual cyclohexane in the obtained massive hydrogenation polystyrene was carried out by GC. Moreover, methyl tertiary butyl ether was not detected. The glass transition temperature for which it asked from DSC measurement was 148 degrees C. Among the toluene solution of concentration 0.5 g/dL, reduced viscosity etasp/C measured at 30 degrees C was 0.45 dL/g, and was a value high enough.

[0048] It introduced into the container made from 5L stainless steel equipped with the mechanical stirring aerofoil and the RIBIHHI mold condensator made from stainless steel set as 10 degrees C, after dissolving Sumi Reiser GS and 0.4g in 1000g of hydrogenation polystyrene cyclohexane solutions obtained in the example 1 of the [example 1 of comparison] reference as a stabilizer. After carrying out the nitrogen purge of the inside of a container, an internal temperature is set as 60 degrees C, internal pressure is adjusted to 52kPa(s) using a vacuum pump, and 750g was made to remove a cyclohexane, stirring. Since it foamed and solidified, the polymer suspended the agitator in the meantime. At this time, polymer concentration was 48 % of the weight. Subsequently, the container was heated at 250 degrees C and the agitator was again rotated with the fluidity of a polymer going up. The cyclohexane was made to remove for 10 minutes, adjusting and stirring internal pressure to 500Pa further using a vacuum pump. After cooling a container to near the ordinary temperature, nitrogen was introduced, and massive hydrogenation polystyrene 102g was obtained from the inside of a container. The hydrogenation polystyrene foamed and solidified had adhered to the container wall.

[0049] It was 3700 ppm when the quantum of the residual cyclohexane in the obtained massive hydrogenation polystyrene was carried out by GC. Moreover, methyl tertiary butyl ether was not detected. The glass transition temperature for which it asked from DSC measurement is 136 degrees C, and the fall of a large glass transition temperature was accepted as compared with the massive hydrogenation polystyrene obtained in the example 1. Among the toluene solution of concentration 0.5 g/dL, reduced viscosity etasp/C measured at 30 degrees C was 0.45 dL/g, and was a value high enough.

[0050] It introduced into the container made from 5L stainless steel equipped with the

mechanical stirring aerofoil and the RIBIHHI mold condensator made from stainless steel set as 10 degrees C, after dissolving Sumi Reiser GS and 0.4g in 1000g of hydrogenation polystyrene cyclohexane solutions obtained in the example 1 of the [example 2 of comparison] reference as a stabilizer. A container is heated at 60 degrees C, and 750g was made to remove a cyclohexane, after carrying out the nitrogen purge of the inside of a container, adjusting and stirring internal pressure to 52kPa(s) using a vacuum pump. Since it foamed and solidified, the polymer suspended the agitator in the meantime. At this time, polymer concentration was 48 % of the weight. Subsequently, the container was heated at 350 degrees C and the agitator was again rotated with the fluidity of a polymer going up. The cyclohexane was made to remove for 10 minutes, adjusting and stirring internal pressure to 500Pa further using a vacuum pump. After cooling a container to near the ordinary temperature, nitrogen was introduced, and massive hydrogenation polystyrene 105g was obtained from the inside of a container. The hydrogenation polystyrene foamed and solidified had adhered to the container wall.

[0051] Among the concentration of 0.5g of the obtained massive hydrogenation polystyrene / toluene solution of dL, reduced viscosity etasp/C measured at 30 degrees C is 0.37 dL/g, and the sharp fall of viscosity was accepted.

[0052] It introduced into the container made from 5L stainless steel equipped with the mechanical stirring aerofoil and the RIBIHHI mold condensator made from stainless steel set as 10 degrees C, after dissolving Irganox1010 [product made from Tiba Speciality Chemicals] 0.8g in 1000g of the hydrogenation copolymer toluene solution obtained in the example 2 of [example 2] reference as a stabilizer. Stirring a toluene solution, contents were heated and boiled at ordinary pressure and toluene 745g was made to remove. At this time, polymer concentration was 75 % of the weight. Subsequently, an internal temperature is set as 230 degrees C, and toluene 60g was made to remove further, adjusting and stirring internal pressure to 25kPa(s) using a vacuum pump. At this time, polymer concentration was 97 % of the weight. Toluene was made to remove for 10 minutes, adjusting and stirring internal pressure to 500Pa further using a vacuum pump with a temperature of 230 degrees C as. After cooling a container to near the ordinary temperature, nitrogen was introduced, and 190g of massive hydrogenation ethylene-dicyclopentadiene copolymers was obtained from the inside of a container.

[0053] It was 190 ppm when the quantum of the residual toluene in the obtained massive hydrogenation ethylene-dicyclopentadiene copolymer was carried out by GC. Moreover, the glass transition temperature for which it asked from DSC measurement was 148 degrees C. Among the toluene solution of concentration 0.5 g/dL, reduced viscosity etasp/c measured at 30 degrees C was 0.45 dL/g, and was a value high enough.

[0054] It introduced into the container made from 5L stainless steel equipped with the mechanical stirring aerofoil and the RIBIHHI mold condensator made from stainless steel set as 10 degrees C, after dissolving Irganox 1010 and 0.8g in 1000g of toluene solutions of the hydrogenation polymer obtained in the example 3 of [example 3] reference as a stabilizer. Stirring a toluene solution, after carrying out the nitrogen purge of the inside of a container, contents were heated and boiled at ordinary pressure and toluene 750g was made to remove. At this time, polymer concentration was 72 % of the weight. Subsequently, an internal temperature is set as 230 degrees C, and toluene 60g was made to remove further, adjusting and stirring internal pressure to 25kPa(s) using a vacuum pump. At this time, polymer concentration was 95 % of the weight. Toluene was made to remove for 10 minutes, adjusting and stirring internal pressure to 500Pa further using a vacuum pump with a temperature of 230 degrees C as. After cooling a container to near the ordinary temperature, nitrogen was introduced, and 180g of

massive hydrogenation polymers was obtained from the inside of a container.

[0055] It was 190 ppm when the quantum of the amount of residual toluene in the obtained massive hydrogenation polymer was carried out by GC. Moreover, the glass transition temperature for which it asked from DSC measurement was 140 degrees C. Among the toluene solution of concentration 0.5 g/dL, reduced viscosity etasp/C measured at 30 degrees C was 0.50 dL/g, and was a value high enough.

[0056] In the [example 4] example 1, the pressure of 8kPa(s) and a three-stage eye was set [Sumi Reiser's GS [the Sumitomo Chemical Co., Ltd. make] addition] to 3kPa(s) for 1.6g and the 2nd step of pressures, and also it experimented similarly, and massive hydrogenation polystyrene 118g was obtained from the inside of a container.

[0057] It was 380 ppm when the quantum of the residual cyclohexane in the obtained massive hydrogenation polystyrene was carried out by GC. Moreover, methyl tertiary butyl ether was not detected. The glass transition temperature for which it asked from DSC measurement was 149 degrees C. Among the toluene solution of concentration 0.5 g/dL, reduced viscosity etasp/C measured at 30 degrees C was 0.48 dL/g, and was a value high enough.

[0058] The annular olefin system polymer obtained in the [example 5] example 1 was set as the resin temperature of 320 degrees C, and the die temperature of 80 degrees C, and the disk substrate which is a typical optical material was fabricated with injection and compression molding. The obtained disk substrate is transparent and colorless, and there was neither curvature nor a surface sink. Moreover, reduced viscosity etasp/C measured at 30 degrees C was 0.44 among the toluene solution of concentration 0.5 g/dL, glass transition temperature was 148 degrees C, and it was a value with both values high enough.

[0059] The annular olefin system polymer obtained in the [example 6] example 1 was set as the resin temperature of 320 degrees C, and the die temperature of 80 degrees C, and the syringe of the disposable syringe which is a typical medical-application ingredient was fabricated with injection and compression molding. The syringe of the obtained syringe was transparent and colorless, and glass transition temperature was 148 degrees C, and was a value high enough.

[Translation done.]

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最終頁に続く

(54)【発明の名称】　環状オレフィン系重合体の製造方法

(57)【要約】
【課題】　耐熱性の低下と分子量の低下が少なく、残留溶剤が少ない環状オレフィン系重合体の製造方法を提供する。
【解決手段】　環状オレフィン系重合体および有機溶剤からなる環状オレフィン系重合体組成物を攪拌しながら、（１）常圧で温度２０℃以上組成物の沸点以下、（２）圧力４ｋＰａ以上７０ｋＰａ以下、温度８０℃以上２５５℃以下、（３）圧力１Ｐａ以上４ｋＰａ未満、温度１９０℃以上２５５℃以下と段階的に加熱減圧し、該有機溶剤を除去する。この方法により耐熱性の低下と分子量の低下が少なく、残留有機溶剤が少ない重合体を得ることができる。

【特許請求の範囲】
【請求項１】　環状オレフィン系重合体および有機溶剤からなる環状オレフィン系重合体組成物を攪拌しながら、（１）常圧で温度２０℃以上組成物の沸点以下、（２）圧力４ｋＰａ以上７０ｋＰａ以下、温度８０℃以上２５５℃以下、（３）圧力１Ｐａ以上４ｋＰａ未満、１９０℃以上２５５℃以下、と段階的に加熱減圧し、該有機溶剤を除去することを特徴とする環状オレフィン系重合体の製造方法。
【請求項２】　該有機溶剤が炭素数５～１４の脂肪族炭化水素、炭素数６～１４の芳香族炭化水素、または炭素数１～１０の含酸素脂肪族炭化水素である請求項１に記載の環状オレフィン系重合体の製造方法。
【請求項３】　該環状オレフィン系重合体の、濃度０．５ｇ／ｄＬのトルエン溶液中３０℃で測定した還元粘度が０．１５ｄＬ／ｇ以上１．５ｄＬ／ｇ以下である請求項１に記載の環状オレフィン系重合体の製造方法。
【請求項４】　請求項１～請求項３のいずれか１項に記載の製造方法によって得られた環状オレフィン系重合体。
【請求項５】　請求項１～請求項３のいずれか１項に記載の製造方法によって得られた環状オレフィン系重合体から主としてなる光学材料。
【請求項６】　請求項１～請求項３のいずれか１項に記載の製造方法によって得られた環状オレフィン系重合体から主としてなる医療材料。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、環状オレフィン系重合体およびその製造方法に関する。さらに詳しくは、環状オレフィン系重合体と有機溶剤からなる環状オレフィン系重合体組成物から、該環状オレフィン系重合体の耐熱性の低下と分子量を低下をおこすことなく該有機溶剤を除去し、該有機溶剤がほとんど残留していない環状オレフィン系重合体の製造方法、およびそれによって得られた環状オレフィン系重合体、および該環状オレフィン系重合体から主としてしてなる成形材料に関するものである。該環状オレフィン系重合体は、光学均質性、高透明性により光ディスク基板をはじめとする光学材料用途、また高透明性、低透湿性による医療材料用途に好適である。
【０００２】
【従来の技術】光ディスク等の光学材料に用いられるプラスチックには、高透明性、光学等方性（低複屈折性）、寸法安定性、耐候性、熱安定性等の様々な特性が要求される。また、記録材料の高密度化の進展に伴い、従来愛用されてきたポリカーボネートやポリメタクリル酸メチルは次に示すような欠点がある。前者は固有複屈折率が大きく成形物に光学異方性が生じやすいこと、後者は吸水率が極めて高いため寸法安定性に乏しく、また耐熱性も低いことである。情報を高密度に記録するほどこれらの欠点は顕著なものとなる。かかる状況を鑑み、ポリカーボネート等の代替材料として環状オレフィン系重合体の開発が盛んに行われている。これらの重合体は、①メタセシス触媒により環状オレフィン等を開環重合した後、重合体に生じる不飽和二重結合を水素化したもの、②チーグラー・ナッタ触媒、あるいはメタロセン触媒により、エチレン、またはプロピレンなどのα－オレフィンと環状オレフィン等とを環状オレフィン等を開環させることなく共重合した後、不飽和二重結合を水素化したもの、③ポリスチレンを主成分とする（共）重合体の芳香族を含む不飽和二重結合を水素化したもの、に大別される。これら重合体は主として溶液系での重合反応、および引き続き行われる水素付加反応によって得られており、反応直後においては環状オレフィン系重合体と有機溶剤からなる環状オレフィン系重合体組成物として得られることが多い。かかる組成物から目的とする環状オレフィン系重合体を得るためには、かかる組成物から有機溶剤を除去することが必要となる。
【０００３】一般にオレフィン重合体と溶剤からなる組成物からかかる溶剤を除去する方法として、Ａ）加圧下または常圧下加熱した重合体組成物をかかる重合体の融点以下、常圧または減圧下の容器中に噴射することによって溶剤を除去する方法（特開昭５７－１３９１０７号公報、ＵＳＰ３５４４５４０等）、Ｂ）容器中で重合体組成物を加熱して溶剤を除去する方法（ＷＯ９９－３２５２５等）が公知である。Ａ）法は脱溶剤が比較的容易である主に結晶性のポリエチレンに適用されており、非晶性である環状ポリオレフィンでは脱溶剤が困難である。一方、Ｂ）法は非晶性ポリオレフインに適用されているが、一般にガラス転移温度の低い重合体のための条件であり、このまま環状オレフィン系重合体に適用した場合は多量の溶剤が残留することが懸念される。また残留溶剤を少なくするために、さらに加熱して組成物の温度を上げて溶剤を除去すると、加熱により該重合体中の熱劣化成分が増え分子量の低下や耐熱性の低下が起こることが懸念される。
【０００４】環状オレフィン系重合体は、光学均質性、高透明性により光ディスク基板をはじめとする光学材料用途に好適である。しかし、該重合体の熱劣化成分は重合体の着色や耐熱性の低下の問題が、また過剰に残留した有機溶剤は該重合体の熱変形温度の低下や、成形時に脱溶剤に伴う反りやひけ等の問題が生ずる。
【０００５】また、環状オレフィン系重合体はその高透明性、低透湿性から、医薬医療用途での容器や包装材として利用も期待されている。該重合体の熱劣化成分は重合体の着色や力学物性の低下の問題が、また過剰に残留した有機溶剤は滲出による周囲への汚染の問題が懸念される。
【０００６】

【発明が解決しようとする課題】本発明は、耐熱性の低下と分子量の低下が少なく、残留溶剤が少ない環状オレフィン系重合体の製造方法、およびその方法によって得られる環状オレフィン系重合体、ならびに該重合体から得られた光学材料および医療材料の提供を目的とする。

【０００７】

【課題を解決するための手段】以上のような状況から耐熱性の低下と分子量の低下が少なく、残留溶剤の少ない環状オレフィン系重合体の製造が必須であり、また望まれている。我々はかかる状況を鑑み鋭意検討した結果、上記環状オレフィン系重合体と有機溶剤からなる環状オレフィン系重合体組成物を、撹拌しながら段階的に減圧および／または加熱することにより、耐熱性の低下がほとんどなく残留溶剤量が著しく少ない環状オレフィン系重合体の製造方法を見出した。かかる製造方法によって得られた環状オレフィン系重合体、および該重合体を主としてなる成形材料は、耐熱性の低下と分子量の低下が少なく、また、残留溶剤量が著しく少ない。よって該成形材料から成形した成形品は反りやひけがなく、さらには溶剤滲出による周囲への汚染の心配が少ない。以上の知見から我々は本発明を提案するに至った。

【０００８】すなわち本発明は、環状オレフィン系重合体および有機溶剤からなる環状オレフィン系重合体組成物を撹拌しながら、（１）常圧で温度２０℃以上組成物の沸点以下、（２）圧力４ｋＰａ以上７０ｋＰａ以下、温度８０℃以上２５５℃以下、（３）圧力１Ｐａ以上４ｋＰａ未満、温度１９０℃以上２５５℃以下、と段階的に加熱減圧し、該有機溶剤を除去することを特徴とする環状オレフィン系重合体の製造方法である。さらに本発明は上記の製造方法により得られた耐熱性の低下が少なく残留有機溶剤の少ない環状オレフィン系重合体を含む。さらに本発明は、上記の製造方法により得られた残留有機溶剤の少ない環状オレフィン系重合体から主としてなる光学材料、医療材料を提供するものである。

【０００９】

【発明の実施の形態】本発明において、用いられる環状オレフィン系重合体としては、①メタセシス触媒により環状オレフィン等を開環重合した後、重合体に生じる不飽和二重結合を水素化した水素化開環重合体、②チーグラー・ナッタ触媒、あるいはメタロセン触媒により、エチレンまたはプロピレンなどのα－オレフィンと環状オレフィン等を環状オレフィン等を開環させることなく共重合した後、必要に応じて不飽和二重結合を水素化した付加型共重合体、③ポリスチレンを主成分とする重合体または共重合体の芳香族を含む不飽和二重結合を水素化した水素化スチレン系重合体および水素化スチレン系共重合体、に大別される。

【００１０】①の水素化開環重合体は前駆体である開環重合体の水素化により得られるものである。開環重合体は、一般に環状オレフィン等をメタセシス触媒の存在下で重合することにより得られる。これらは、特開昭６０－２６０２４号公報、特開昭６３－２１８７２６号公報、特開平２－１３３４１３号公報、特開平３－１０９４１８号公報等に開示されている。用いられる単量体として、ノルボルネン、５－フェニルノルボルネン、テトラシクロ［４，４，０，$1^{2,5}$，$1^{7,10}$］－３ドデセン、８－フェニルテトラシクロ［４，４，０，$1^{2,5}$，$1^{7,10}$］－３ドデセン等の環状モノエンや、シクロペンタジエン、ジシクロペンタジエン、ノルボルナジエン、５－エチリデンノルボルネン、８－エチリデンテトラシクロ［４，４，０，$1^{2,5}$，$1^{7,10}$］－３－ドデセン、８－イソプロピリデンテトラシクロ［４，４，０，$1^{2,5}$，$1^{7,10}$］－３－ドデセン等の環状ジエンが好ましく用いられる。中でも原料の入手性およびポリマーの耐熱性を勘案すると、ノルボルネン、テトラシクロ［４，４，０，$1^{2,5}$，$1^{7,10}$］－３ドデセン、ジシクロペンタジエンが特に好ましい。

【００１１】得られた開環重合体には不可避的にＣ＝Ｃ二重結合が含まれる。Ｃ＝Ｃ二重結合を含む重合体は熱化学安定性に乏しく、実用に耐えない。そのために、開環重合体は水素化触媒の存在下でさらに水素化する必要がある。開環重合体の水素化方法は特には限定されず、Ｃ＝Ｃ二重結合を効率よく水素化できる方法であれば良い。一般には水素化触媒の存在下で不活性溶媒中、水素加圧下で水素化を行う。不活性溶媒にはヘキサン、ヘプタン、オクタン、ドデカン、シクロヘキサン、シクロヘプタン、シクロデカン、メチルシクロヘキサン等の炭素数５～１４の脂肪族炭化水素；ベンゼン、トルエン、キシレン、エチルベンゼン等の炭素数６～１４の芳香族炭化水素が好適に用いられ、これらの内、シクロヘキサン、メチルシクロヘキサン、トルエンが最も好ましく用いられる。水素化触媒としてはニッケル、パラジウム、白金、コバルト、ルテニウム、ロジウム等のＶＩＩＩ属の金属またはその化合物をカーボン、アルミナ、シリカ、シリカアルミナ、珪藻土等の多孔性担体に担持した固体触媒あるいはバナジウム、クロム、マンガン、鉄、ルテニウム、コバルト、ニッケル、パラジウム等、ＩＶ属～ＶＩＩＩ属のハロゲン化物、アセチルアセトネート錯体、カルボキシレート錯体、ナフテート錯体、トリフルオロアセテート錯体、ステアレート錯体等の均一触媒が挙げられる。これらのなかで、均一触媒を用いるのが特に好ましい。

【００１２】②の付加型共重合体は、エチレンまたはプロピレンなどのα－オレフィンと環状オレフィンとを環状オレフィンを開環させることなく共重合したものでる。これらは特開昭６０－１６８７０８号公報、特開昭６１－１１５９１６号公報、特開昭６１－２２１２０６号公報、特開昭６１－２９２６０１号公報等に開示されている。環状オレフィンとしては、ノルボルネン、５－フェニルノルボルネン、テトラシクロ［４，４，０，１

^{2,5}，$1^{7,10}$］－３ドデセン、８－フェニルテトラシクロ［４，４，０，$1^{2,5}$，$1^{7,10}$］－３ドデセン等の環状モノエンや、シクロペンタジエン、ジシクロペンタジエン、ノルボルナジエン、５－エチリデンノルボルネン、８－エチリデンテトラシクロ［４，４，０，$1^{2,5}$，$1^{7,10}$］－３－ドデセン、８－イソプロピリデンテトラシクロ［４，４，０，$1^{2,5}$，$1^{7,10}$］－３－ドデセン等の環状ジエンが好適に用いられる。中でも原料の入手性およびポリマーの耐熱性を勘案すると、ノルボルネン、テトラシクロ［４，４，０，$1^{2,5}$，$1^{7,10}$］－３－ドデセン、ジシクロペンタジエンが特に好適である。その内、環状ジエンを用いた場合には生成重合体がＣ＝Ｃ二重結合を含むために、上述したように水素化開環重合体の製造方法と同様に付加重合体をさらに水素化することが好ましい。

【００１３】また、α－オレフィンとしては、プロピレン、１－ブテン、１－ペンテン、１－ヘキセン、４－メチル－１－ペンテン、１－ヘプテン、１－ドデセン等の炭素数３～１４のα－オレフィンが用いられる。環状オレフィンと共重合する単量体としては反応性の上からエチレンが最も好ましいが、その他プロピレンも好ましく用いられる。これらは単独で用いても２種類以上組み合わせても良い。かかる付加重合体は、一般にチーグラー・ナッタ触媒、あるいはメタロセン触媒の存在下において容易に合成することができる。

【００１４】③の水素化スチレン系重合体および水素化スチレン系共重合体は、ポリスチレンを主成分とする重合体、またはポリスチレン系共重合体の芳香族を含む不飽和二重結合に水素付加反応を施したものである。これらは一般にスチレン系重合体および／またはスチレン系共重合体を水素化することにより容易に得られる。スチレン系重合体に用いられるスチレン系単量体としては、スチレン、α－メチルスチレン、ｐ－メチルスチレン、ビニルナフタレン等が挙げられる。この内、入手性、ポリマー物性上からスチレンが最も好ましく、その重合体がポリスチレンである。

【００１５】一方、スチレン系重合体の共重合成分としては、１，３－ブタジエン、イソプレン、２，３－ジメチルブタジエン、２，３－ペンタジエン、２，３－ヘキサジエン等のジエン類が好ましく用いられる。これらの共重合成分を導入することにより、目的とする環状重合体の透明性を損なうことなく力学物性を著しく向上させることができる。これらの中でも重合活性、経済性の面からイソプレン、１，３－ブタジエンが好ましく用いられる。これらは単独で用いてもよいし、２種類以上併用して用いてもよい。かかるスチレン－共役ジエン共重合体における共役ジエン成分の割合は、１重量％以上３０重量％以下の範囲にあることが好ましい。より好ましくは共役ジエン成分が２重量％以上２５重量％以下の範囲である。共役ジエン成分の割合が１重量％以下では耐衝撃性等の力学特性を向上させることができず、３０重量％を超えると環状オレフィン系重合体の耐熱性を損なうだけでなく、透明性も損なうため好ましくない。

【００１６】これらのスチレン系重合体およびスチレン系共重合体の製造法は特に限定はなく、一般のラジカル重合法、アニオン重合法、カチオン重合法等が好ましく用いられる。また、スチレン系重合体に共重合成分を導入したスチレン系共重合体の結合様式として、ランダム共重合体、ブロック共重合体、ラジアルブロック共重合体等が挙げられる。ラジアルブロック共重合体とはブロック共重合体の内ラジアル形状を持つものであり、ラジアル形状とは数本のポリマー鎖が中心から放射状に伸びたような形状を示す。これらの内、耐熱性を重視する場合にはブロック共重合体が、また成形時の流動性を重視する場合にはラジアルブロック共重合体が特に好ましい。これらは用途に応じて適宜判断して採用すれば良い。

【００１７】スチレン系重合体およびスチレン系共重合体の水素化方法は特には限定されず、芳香族ならびにＣ＝Ｃ二重結合を効率よく水素化できる方法であれば良い。一般には水素化触媒の存在下で不活性溶媒中、水素加圧下、高温で水素化を行う。不活性溶媒にはヘキサン、ヘプタン、オクタン、ドデカン、シクロヘキサン、シクロヘプタン、シクロデカン、メチルシクロヘキサン等の炭素数５～１４の脂肪族炭化水素が好適に用いられ、これらの内、シクロヘキサン、メチルシクロヘキサンが最も好適に用いられる。水素化触媒としてはニッケル、パラジウム、白金、コバルト、ルテニウム、ロジウム等のＶＩＩＩ属の金属またはその化合物をカーボン、アルミナ、シリカ、シリカアルミナ、珪藻土等の多孔性担体に担持した固体触媒あるいはバナジウム、クロム、マンガン、鉄、ルテニウム、コバルト、ニッケル、パラジウム等、ＩＶ属～ＶＩＩＩ属のハロゲン化物、アセチルアセトネート錯体、カルボキシレート錯体、ナフテート錯体、トリフルオロアセテート錯体、ステアレート錯体等の均一触媒が挙げられる。これらの内、ニッケル、パラジウム、白金をシリカ、シリカアルミナ、珪藻土に担持したものが活性が高く好ましく用いられる。これら水素化触媒は単独で用いても、組み合わせて用いても良い。

【００１８】該重合体の分子量は、分子量を表す代表的な尺度である還元粘度（ηｓｐ／Ｃ）を用いて表すことにする。成形材料の機械的強度ならびに成形加工性を勘案すると、濃度０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度で０．１５ｄＬ／ｇ以上１．５ｄＬ／ｇ以下の範囲のものが好ましく、より好ましくは０．２ｄＬ／ｇ以上１．０ｄＬ／ｇの範囲、さらに好ましくは０．３ｄＬ／ｇ以上０．８ｄＬ／ｇである。平均分子量が０．１５ｄＬ／ｇより低いと機械的強度が不足し、１．５ｄＬ／ｇより高いと溶融粘度が高すぎて流動

性が不足し成形が困難になり好ましくない。

【００１９】本発明における環状オレフィンと有機溶剤からなる環状オレフィン系重合体組成物とは、上記①、②、③の溶液系による合成の後に触媒残渣等金属灰分を除去した該環状オレフィン重合体と有機溶剤からなる溶液である。

【００２０】該有機溶剤とは、上記①、②、③の合成過程で用いられた有機溶剤であり、ヘキサン、ヘプタン、オクタン、ドデカン、シクロヘキサン、シクロヘプタン、シクロデカン、メチルシクロヘキサン等の炭素数５～１４の脂肪族炭化水素；ベンゼン、トルエン、キシレン、エチルベンゼン等の炭素数６～１４の芳香族炭化水素；メタノール、エタノール、ジエチルエーテル、メチルターシャリーブチルエーテル、テトラヒドロフラン、フラン、ピラン等の炭素数１～１０の含酸素脂肪族炭化水素、またそれら任意の混合物であってもよい。それらの中でもトルエン、シクロヘキサン、メチルシクロヘキサン、メチルターシャリーブチルエーテルが好ましく挙げられる。

【００２１】本発明における環状オレフィン系重合体組成物は、ロータリーエバポレーター等であらかじめ濃縮して用いても、また、上記有機溶剤の項で挙げた有機溶剤で希釈しても良いが、環状オレフィン系重合体５～６０重量%、有機溶剤４０～９５重量%からなる組成物、好ましくは環状オレフィン系重合体１０～５０重量%、有機溶剤５０～９０重量%からなる組成物、さらに好ましくは環状オレフィン系重合体１５～４０重量%、有機溶剤６０～８５重量%からなる組成物である。環状オレフィン重合体の組成が６０重量%を超えると、環状オレフィン系重合体組成物の流動性が乏しく、またかかる組成が５重量%未満では環状オレフィン系重合体の収率が低く、ともに好ましくない。

【００２２】本発明における、熱劣化による分子量の低下をさらに効果的に抑制するため、環状オレフィン共重合体中に熱分解防止のための安定剤を添加することが好ましい。安定剤としては一般に市販されているヒンダードフェノール系安定剤、ラクトン系安定剤、ホスファイト系安定剤等何れも使用可能であり、またこれらの任意の組み合わせも使用可能である。中でも好ましくはヒンダードフェノール系安定剤、より好ましくはヒンダードフェノール基含有アクリレート化合物の安定剤が好ましい。かかる安定剤は重合体に対して５００ｐｐｍ以上５００００ｐｐｍ以下、好ましくは１０００ｐｐｍ以上３００００ｐｐｍ以下、さらに好ましくは２０００ｐｐｍ以上２００００ｐｐｍ以下の範囲で用いられる。かかる安定剤が５００００ｐｐｍ以上であると環状オレフィン系重合体のヘイズや着色の原因になり、５００ｐｐｍ以下では効果が不十分となるため共に好ましくない。

【００２３】本発明における、段階的に該有機溶剤を除去することとは、かかる環状オレフィン系重合体組成物

を攪拌しながら、（１）常圧で温度２０℃以上組成物の沸点以下、（２）圧力４ｋＰａ以上７０ｋＰａ以下、温度８０℃以上２５５℃以下、（３）圧力１Ｐａ以上４ｋＰａ以下、温度１９０℃以上２５５℃以下、と段階的に加熱減圧し、該有機溶剤を蒸発させて除去することである。

【００２４】（１）は、最も溶剤が除去される段階であり、大気圧下かかる組成物の沸点以下で行うことが好ましい。減圧下で行うと該重合体組成物が発泡しながら固化し、攪拌できなくなるばかりか溶剤が発泡体中に残存しやすく、好ましくない。温度はかかる組成物の沸点マイナス１０℃以上組成物の沸点以下が好ましく、組成物の沸点マイナス５℃以上沸点以下がより好ましい。温度がかかる組成物の沸点マイナス１０℃未満では溶剤除去効率が低くなるため好ましくない。濃縮後の、組成物中に含まれる重合体濃度は５０重量%以上８５重量%以下が好ましく、より好ましくは６０重量%以上８０重量%以下である。重合体濃度が８５重量%を超えると粘度が高くなるか、または固化することによって攪拌できなくなり、重合体濃度が６０重量%未満では第２段階での溶剤除去効率が低くなる、あるいは第２段階で発泡、固化しやすく共に好ましくない。

【００２５】（２）は溶剤の大部分が除去される段階であり、圧力４ｋＰａ以上７０ｋＰａ以下、温度８０℃以上２５５℃以下が好ましい。圧力が７０ｋＰａを超えると溶剤が除去されにくく、圧力が４ｋＰａ未満では該溶剤が発泡、固化しやすく好ましくない。一方、温度が２５５℃を超えると環状オレフィン系重合体の熱劣化成分が増え、また８０℃未満では溶剤が除去されにくいだけでなく、かかる重合体溶液の粘度が高すぎて攪拌できなくなり好ましくない。かかる濃縮段階後の、組成物中に含まれる重合体濃度は８５重量%より大きく９９．５重量%以下が好ましく、より好ましくは９０重量%以上９９重量%以下である。重合体濃度が９９．５重量%を超えると、（１）の段階と同じく粘度が高くなるかまたは固化することによって攪拌ができなくなり、重合体濃度が８５重量%未満では第３段階での溶媒除去効率が低くなり、好ましくない。

【００２６】（３）は溶剤が高度に除去される段階であり、圧力１Ｐａ以上４ｋＰａ以下、温度１９０℃以上２５５℃以下が好ましい。圧力が４ｋＰａを超えると溶剤が除去されにくく、また１Ｐａ未満では圧力を調整する機器が高価となるため経済的に現実的でなく、好ましくない。一方、温度が２５５℃を超えると環状オレフィン系重合体の熱劣化成分が増え、また１９０℃未満では溶剤が除去されにくいだけでなく、かかる重合体溶液の粘度が高すぎて攪拌できなくなり好ましくない。かかる溶剤除去について、環状オレフィン系重合体溶液を攪拌しながら行うことは、溶剤の拡散という観点からも好適である。また、（２）、（３）の段階について温度が２３

０℃以上の継続時間は３０分以内が好ましく、さらに２０分以内が好ましい。温度が２３０℃以上の継続時間が３０分以上では熱劣化が著しく生じるため好ましくない。

【００２７】かくして得られた環状オレフィン系重合体の残留有機溶量剤は５００ｐｐｍ以下が好ましく、さらに好ましくは２００ｐｐｍ以下である。残留有機溶剤量が５００ｐｐｍ以上ではガラス転移温度の低下がおよそ５℃以上となり耐熱性の観点から好ましくない。また、熱劣化に伴うηｓｐ／Ｃの低下は０．０６以下が好ましく、さらに好ましくは０．０３以下である。ηｓｐ／Ｃの低下が０．０６を超えると本来設計した力学物性を達成できなくなり好ましくない。ここで言うηｓｐ／Ｃとは環状オレフィン系重合体の０．５ｇ／ｄＬトルエン溶液の３０℃における還元粘度である。

【００２８】かくして得られた残留有機溶剤の少ない環状オレフィン系重合体からなる光学材料ならびに医療材料は、射出成形、押し出し成形等の溶融成形法等、公知の成形法により成形できる。特に射出成形は光ディスク基板の製造に好適に用いることができる。

【００２９】

【発明の効果】本発明によれば、熱劣化が少なく、残留有機溶剤の少ない環状オレフィン系重合体およびその光学材料、医療材料が得られる。その結果、残留有機溶剤の少ない環状オレフィン系重合体は、製品最終工程または成形時に乾燥等脱溶剤をする必要がない。また得られた成形材料について残存溶剤による熱変形温度の低下にともなう耐熱性の低下がなく、また脱溶剤に伴う寸法変化等の物理的不安定性、環境負荷などがない優れた、光学材料ならびに医療材料を提供することができる。

【００３０】

【実施例】以下に実施例により本発明を詳述する。但し、本発明はこれら実施例に何ら限定されるものではない。

【００３１】シクロヘキサン、トルエン、スチレン、イソプレン、ジシクロペンタジエン（ＤＣＰＤ）は、すべて蒸留精製を行い充分に乾燥したものを用いた。

【００３２】参考例で測定用に用いた環状オレフィン系重合体は以下のように単離した。すなわち、環状オレフィン系重合体組成物のごく一部をイソプロパノール中に再沈して得た該重合体スラリーを濾過、６０℃で５時間減圧乾燥し、フレーク状の環状オレフィン系重合体を得た。実施例で行った上記（１）～（３）の段階の内、（２）、（３）の段階において温度が２３０℃以上の継続時間はいずれも１０分以上１５分以下の範囲であった。

【００３３】実施例、参考例、比較例で行った測定項目は以下の方法で測定した。

１）スチレン分率、ＤＣＰＤ分率、水素化率：ＪＥＯＬ製　ＥＸ－２７０型核磁気共鳴吸収装置を使用し、重水素化クロロホルムを溶媒とし、テトラメチルシランを内部標準として常温で^{1}Ｈ－ＮＭＲ測定を行い定量した。

２）ガラス転移温度（Ｔｇ）：ＴＡ　Ｉｎｓｔｒｕｍｅｎｔｓ製　２９２０型ＤＳＣを使用し、昇温速度は２０℃／分で測定した。

３）還元粘度：濃度０．５ｇ／ｄＬのトルエン溶液の、３０℃における還元粘度（ηｓｐ／Ｃ）を測定した。

４）残存溶剤量：島津製作所（株）製ＧＣ－５Ａ型ガスクロマトグラフィー（ＧＣ）を用い、下記のようにサンプルを調製して測定した。残存溶剤がシクロヘキサンの場合、０．５ｇの重合体を分析用トルエン［関東化学（株）製ＨＰＬＣグレード］９．５ｇに溶解させ、得られたトルエン溶液を分析用イソプロパノール［関東化学（株）製ＨＰＬＣグレード］２０ｇに加えて重合体成分を再沈させた。得られた混合物を濾過し濾液をサンプルとした。溶剤がトルエンの場合、重合体を分析用シクロヘキサン［関東化学（株）製ＨＰＬＣグレード］に溶解させるほかは、同様にしてサンプルを調製した。

５）光線透過率：島津製作所（株）製紫外可視分光器（ＵＶ－２４０）を使用した。

６）ヘイズ値：日本電色工業（株）製自動デジタルヘイズメーターＵＤＨ－２０Ｄを使用した。

７）重合体濃度：参考例にて作成した重合体溶液の一部を取り、加熱して溶剤を除去して重合体の初期濃度を算出した。この値を元に除去した溶剤量から算出した。

【００３４】［参考例１］ＢＡＳＦ・ＡＧ製ポリスチレンＧＰ１５８Ｋをシクロヘキサン溶剤中、触媒としてシリカアルミナ担持ニッケル触媒［Ａｌｄｒｉｃｈより購入、ニッケル担持率６５重量％］を用い、以下のようにして水素化反応を行った。

【００３５】反応容器には電磁攪拌翼付き容量１０Ｌのステンレス製オートクレーブを用いた。容器内に該ポリスチレン７５０ｇ、シクロヘキサン［和光純薬工業（株）より購入］２２００ｇ、メチルターシャリーブチルエーテル［関東科学（株）より購入］１５００ｇ、該シリカアルミナ担持ニッケル触媒１１８ｇを仕込み、容器内を窒素ガス、次いで水素ガスで置換した後、１８０℃、水素圧１０ＭＰａで１６０分、水素化反応を行った。容器を常温付近まで冷却した後、容器内を常圧に戻し、さらに容器内を窒素置換して、シリカアルミナ担持ニッケル触媒を含む水素化ポリスチレン、シクロヘキサン溶液を得た。かかる溶液を０．４ＭＰａの窒素加圧下、細孔径０．１μｍのメンブレンフィルターで濾過してシリカアルミナ担持ニッケル触媒を除去し、無色透明の水素化ポリスチレンシクロヘキサン溶液４２００ｇを得た。

【００３６】得られた水素化ポリスチレンシクロヘキサン溶液の一部を採取して各種分析を行った。^{1}Ｈ－ＮＭＲ分析から、水素化率は９９．０％であった。ＤＳＣ測定からガラス転移温度は１４８℃であった。濃度０．５

ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／Ｃは０．４７ｄＬ／ｇであり、充分に高い値であった。

【００３７】［参考例２］メタロセンにイソプロピリデン－（９－フルオレニル）（シクロペンタジエニル）ジルコニウムジクロリド[^{i}Ｐｒ（Ｃｐ）（Ｆｌｕ）$ZrCl_2$、文献Ｊ．Ａ．Ｅｗｅｎ　ｅｔ　ａｌ，Ｊ．Ａｍ．Ｃｈｅｍ．Ｓｏｃ．，ｖｏｌ　１１０，６２５５－６２６６（１９８８）に従い合成］、助触媒に東ソー・アクゾ（株）製トリチルテトラキス（ペンタフルオロフェニル）ボレート（$[(C_6H_5)_3C]^+[B(C_6F_5)_4]^-$）、アルキル化剤に東ソー・アクゾ（株）製トリイソブチルアルミニウムを用い、以下のようにしてエチレンとＤＣＰＤとの共重合反応、水素化反応、触媒除去を行った。

【００３８】反応には電磁攪拌翼付容量３Ｌのステンレス製オートクレーブを用いた。容器内を窒素ガスで置換した後、容器内にトルエン１３２０ｇ、ＤＣＰＤ１８１ｇおよびトリイソブチルアルミニウム溶液（濃度１Ｍのｎ－ヘキサン溶液）１８ｍＬを仕込んだ。次に温度を４０℃に上げた後、容器内をエチレンで充分に置換し、エチレンを溶解飽和させた。続いて２５７ｍｇの$[(C_6H_5)_3C]^+[B(C_6F_5)_4]^-$および１２２ｍｇの^{i}Ｐｒ（Ｃｐ）（Ｆｌｕ）$ZrCl_2$を加え重合を開始させた。重合中、容器内のエチレン圧力が１気圧を保持するようエチレンを供給し続け、同時にエチレンの供給量に対して当モル量のＤＣＰＤを連続して供給し続けた。重合を開始して１４０分後、微量のイソプロパノールを添加して反応を終了させ、共重合体組成物１７５０ｇを得た。反応の間に供給されたエチレン量は９７ｇ、ＤＣＰＤ量は１６８ｇであった。

【００３９】得られた共重合体組成物の一部を採取して各種分析を行った。^{1}Ｈ－ＮＭＲ分析から、ＤＣＰＤ成分の組成比は４３ｍｏｌ％であった。ＤＳＣ測定からガラス転移温度は１５２℃であった。濃度０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／Ｃは０．７０ｄＬ／ｇであり、充分に高い値であった。

【００４０】得られた共重合体組成物にコバルトトリスアセチルアセトネート錯体３．０ｇとトリイソブチルアルミニウム溶液（濃度１Ｍのｎ－ヘキサン溶液）２４ｍＬの混合物をさらに添加し、１１０℃、水素圧４ＭＰａ、１２０分、水素化反応を行い、黄色で透明な水素化共重合体組成物を得た。かかる水素化共重合体組成物を攪拌しながら１００℃で乳酸３１．８ｇおよび水３．２ｇからなる乳酸水溶液を添加し、同温度で１２０分攪拌することにより均一触媒を凝集させ、濁った桃色の水素化共重合体組成物を得た。かかる桃色の水素化共重合体組成物を細孔径０．４５μｍのメンブランフィルターを用い、０．４ＭＰａの窒素圧で濾過を行ったところ無色透明の水素化共重合体トルエン溶液１５２０ｇを得た。

【００４１】かかる水素化共重合体トルエン溶液の一部を採取して各種分析を行った。^{1}Ｈ－ＮＭＲ分析から、水素化率は９９．９％以上であった。ＤＳＣ測定からガラス転移温度は１４９℃であった。濃度０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／Ｃは０．４８ｄＬ／ｇであり、充分に高い値であった。

【００４２】［参考例３］３Ｌのステンレス製反応容器に８－エチリデンテトラシクロ［４．４．０．$1^{2.5}$．$1^{7.10}$］－３－ドデセン２８５ｇ、トルエン１１００ｇ、１－ヘキセン４．２ｇ、トリエチルアミン７．５ｇ、トリイソブチルアルミニウム１５ｇを加え、さらに四塩化チタン２．８ｇを添加し、－１０℃で１２０分重合を行い、開環重合体を得た。得られた溶液を少量分取して、常法により精製した重合体の０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／Ｃは０．６５ｄＬ／ｇであり、ＤＳＣを用いて測定したガラス転移温度（Ｔｇ）は１８６℃であった。

【００４３】得られた反応容器に１００℃で乳酸７．８ｇおよび水１．０ｇを攪拌しながら添加して、同温で１２０分反応させた。反応液は黒褐色から黒色の濁ったスラリーに変色した。該スラリーを引き続き濾過処理にかけた。濾液を塩基性アルミナを用いて吸着処理をして透明の処理液を得た。かくして得られた溶液を大量のエタノールに添加して、析出した沈殿を濾別、乾燥して無色のフレークを得た。

【００４４】得られたフレーク状固体を５Ｌステンレス製オートクレーブ中に導入した１１００ｇのトルエンに溶解した。該溶液を入れたオートクレーブ中の空気を充分に窒素ガスで置換した。該溶液にトリス（アセチルアセトナート）コバルト３．０ｇおよびトリイソブチルアルミニウム４．８ｇを添加し、水素圧４．４ＭＰａで１２０分間水素付加反応を行い、反応液を得た。該反応溶液を少量分取して、常法により精製したポリマーの水素化率は、^{1}Ｈ－ＮＭＲスペクトルから９９．９％以上であった。また、０．５ｇ／ｄＬのトルエン溶液を用いて３０℃で測定した還元粘度ηｓｐ／Ｃは０．５５ｄＬ／ｇであり、ＤＳＣを用いて測定したガラス転移温度（Ｔｇ）は１４０℃であった。

【００４５】得られた反応液に１００℃で乳酸１７．６ｇおよび水１．８ｇを含む乳酸水溶液を攪拌しながら添加し、同温で１２０分反応させた。反応液は黒褐色からピンク色の濁ったスラリーに変色した。該スラリーを引き続き濾過にかけた。得られた濾液を塩基性アルミナを用いて吸着処理をして、無色透明の水素化重合体トルエン溶液を得た。

【００４６】［実施例１］参考例１で得られた水素化ポリスチレンシクロヘキサン溶液１０００ｇに安定剤としてスミライザーＧＳ［住友化学工業（株）製］０．４ｇを溶解させた後、機械式攪拌翼、１０℃に設定したステンレス製リービッヒ型冷却器を備えた３Ｌステンレス製

容器に導入した。容器内を窒素置換した後、かかるポリスチレン溶液を撹拌しながら、常圧で内容物を加熱して沸騰させ、シクロヘキサン８５０ｇを除去させた。この時点で重合体濃度は８０重量%であった。ついで内温を２３０℃に設定し、真空ポンプを用いて内圧を２５ｋＰａに調節し、撹拌しながらシクロヘキサンを２８ｇ除去させた。この時点で重合体濃度は９８重量%であった。容器を２３０℃のまま真空ポンプを用いてさらに内圧を５００Ｐａに調節し、撹拌しながら１０分間シクロヘキサンを除去させた。容器を常温近くまで冷却した後窒素を導入し、容器内から塊状の水添ポリスチレン１２０ｇを得た。

【００４７】得られた塊状水素化ポリスチレンの中の残存シクロヘキサンをＧＣで定量したところ、１８０ｐｐｍであった。また、メチルターシャリーブチルエーテルは検出されなかった。ＤＳＣ測定から求めたガラス転移温度は１４８℃であった。濃度０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／Ｃは０．４５ｄＬ／ｇであり、充分に高い値であった。

【００４８】［比較例１］参考例１で得られた水素化ポリスチレンシクロヘキサン溶液１０００ｇに安定剤としてスミライザーＧＳ、０．４ｇを溶解させた後、機械式撹拌翼、１０℃に設定したステンレス製リービッヒ型冷却器を備えた５Ｌステンレス製容器に導入した。容器内を窒素置換した後内温を６０℃に設定し、真空ポンプを用いて内圧を５２ｋＰａに調節し、撹拌しながらシクロヘキサンを７５０ｇを除去させた。この間ポリマーは発泡して固化したため、撹拌機を停止した。この時点で重合体濃度は４８重量%であった。ついで容器を２５０℃に加熱し、ポリマーの流動性が上がるのと共に撹拌機をふたたび回転させた。真空ポンプを用いてさらに内圧を５００Ｐａに調節し、撹拌しながら１０分間シクロヘキサンを除去させた。容器を常温近くまで冷却した後窒素を導入し、容器内から塊状の水素化ポリスチレン１０２ｇを得た。容器内壁には発泡して固化した水素化ポリスチレンが付着していた。

【００４９】得られた塊状水素化ポリスチレンの中の残存シクロヘキサンをＧＣで定量したところ、３７００ｐｐｍであった。また、メチルターシャリーブチルエーテルは検出されなかった。ＤＳＣ測定から求めたガラス転移温度は１３６℃で、実施例１で得られた塊状水素化ポリスチレンと比較して大幅なガラス転移温度の低下が認められた。濃度０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／Ｃは０．４５ｄＬ／ｇであり、充分に高い値であった。

【００５０】［比較例２］参考例１で得られた水素化ポリスチレンシクロヘキサン溶液１０００ｇに安定剤としてスミライザーＧＳ、０．４ｇを溶解させた後、機械式撹拌翼、１０℃に設定したステンレス製リービッヒ型冷却器を備えた５Ｌステンレス製容器に導入した。容器内を窒素置換した後、容器を６０℃に加熱し、真空ポンプを用いて内圧を５２ｋＰａに調節し、撹拌しながらシクロヘキサンを７５０ｇを除去させた。この間ポリマーは発泡して固化したため、撹拌機を停止した。この時点で重合体濃度は４８重量%であった。ついで容器を３５０℃に加熱し、ポリマーの流動性が上がるのと共に撹拌機をふたたび回転させた。真空ポンプを用いてさらに内圧を５００Ｐａに調節し、撹拌しながら１０分間シクロヘキサンを除去させた。容器を常温近くまで冷却した後窒素を導入し、容器内から塊状の水素化ポリスチレン１０５ｇを得た。容器内壁には発泡して固化した水素化ポリスチレンが付着していた。

【００５１】得られた塊状水素化ポリスチレンの、濃度０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／Ｃは０．３７ｄＬ／ｇであり、粘度の大幅な低下が認められた。

【００５２】［実施例２］参考例２で得られた水素化共重合体トルエン溶液の内、１０００ｇに安定剤としてＩｒｇａｎｏｘ１０１０［チバ・スペシャリティー・ケミカルス（株）製］０．８ｇを溶解させた後、機械式撹拌翼、１０℃に設定したステンレス製リービッヒ型冷却器を備えた５Ｌステンレス製容器に導入した。トルエン溶液を撹拌しながら、常圧で内容物を加熱して沸騰させ、トルエン７４５ｇを除去させた。この時点で重合体濃度は７５重量%であった。ついで内温を２３０℃に設定し、真空ポンプを用いて内圧を２５ｋＰａに調節し、撹拌しながらさらにトルエン６０ｇを除去させた。この時点で重合体濃度は９７重量%であった。温度２３０℃のまま真空ポンプを用いてさらに内圧を５００Ｐａに調節し、撹拌しながら１０分間トルエンを除去させた。容器を常温近くまで冷却した後窒素を導入し、容器内から塊状の水素化エチレン－ジシクロペンタジエン共重合体１９０ｇを得た。

【００５３】得られた塊状水素化エチレン－ジシクロペンタジエン共重合体中の残存トルエンをＧＣで定量したところ、１９０ｐｐｍであった。また、ＤＳＣ測定から求めたガラス転移温度は１４８℃であった。濃度０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／ｃは０．４５ｄＬ／ｇであり、充分に高い値であった。

【００５４】［実施例３］参考例３で得られた水素化重合体のトルエン溶液１０００ｇに安定剤としてＩｒｇａｎｏｘ１０１０、０．８ｇを溶解させた後、機械式撹拌翼、１０℃に設定したステンレス製リービッヒ型冷却器を備えた５Ｌステンレス製容器に導入した。容器内を窒素置換した後、トルエン溶液を撹拌しながら、常圧で内容物を加熱して沸騰させ、トルエン７５０ｇを除去させた。この時点で重合体濃度は７２重量%であった。ついで内温を２３０℃に設定し、真空ポンプを用いて内圧を２５ｋＰａに調節し、撹拌しながらさらにトルエン６０

ｇを除去させた。この時点で重合体濃度は９５重量％であった。温度２３０℃のまま真空ポンプを用いてさらに内圧を５００Ｐａに調節し、撹拌しながら、１０分間トルエンを除去させた。容器を常温近くまで冷却した後窒素を導入し、容器内から塊状の水素化重合体１８０ｇを得た。

【００５５】得られた塊状水素化重合体中の残存トルエン量をＧＣで定量したところ、１９０ｐｐｍであった。また、ＤＳＣ測定から求めたガラス転移温度は１４０℃であった。濃度０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／Ｃは０．５０ｄＬ／ｇであり、充分に高い値であった。

【００５６】［実施例４］実施例１においてスミライザーＧＳ［住友化学工業（株）製］の添加量を１．６ｇ、２段階目の圧力を８ｋＰａ、３段階目の圧力を３ｋＰａとした他は同様に実験を行い、容器内から塊状の水添ポリスチレン１１８ｇを得た。

【００５７】得られた塊状水添ポリスチレンの中の残存シクロヘキサンをＧＣで定量したところ、３８０ｐｐｍであった。また、メチルターシャリーブチルエーテルは検出されなかった。ＤＳＣ測定から求めたガラス転移温度は１４９℃であった。濃度０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／Ｃは０．４８ｄＬ／ｇであり、充分に高い値であった。

【００５８】［実施例５］実施例１において得られた環状オレフィン系重合体を、樹脂温度３２０℃、金型温度８０℃に設定して射出・圧縮成形により、代表的な光学材料であるディスク基板を成形した。得られたディスク基板は無色透明であり、反りやひけはなかった。また濃度０．５ｇ／ｄＬのトルエン溶液中、３０℃で測定した還元粘度ηｓｐ／Ｃは０．４４、ガラス転移温度は１４８℃であり、両方の値とも充分に高い値であった。

【００５９】［実施例６］実施例１において得られた環状オレフィン系重合体を、樹脂温度３２０℃、金型温度８０℃に設定して射出・圧縮成形により、代表的な医療用材料である使い捨て注射器のシリンジを成形した。得られた注射器のシリンジは無色透明であり、ガラス転移温度は１４８℃であり充分に高い値であった。

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